Radiation-induced grafting copolymerization of resin onto the surface of silica extracted from rice husk ash for adsorption of gadolinium

H.M.H. Gad [a], Mostafa M. Hamed [a], H.M.M. Abo Eldahab [a,*], M.E. Moustafa [b], S.A. El-Reefy [a]

[a] Hot Laboratories and Waste Management Center, Atomic Energy Authority, 13759 Cairo, Egypt
[b] Chemistry Department, Benha University, Cairo, Egypt

ABSTRACT

In this study, novel adsorbents were prepared, characterized and investigated for adsorption of gadolinium as one of rare earth elements. The first adsorbent is rice husk ash (RHA), the second is poly(acrylamide/acrylic acid/sodium styrene sulfonate) resin (P), the third and fourth adsorbents were the prepared resin grafted on the surface of the silica powder (poly(acrylamide/acrylic acid/sodium styrene sulfonate/silica powder) (P-SP) and gel form (poly(acrylamide/acrylic acid/sodium styrene sulfonate/silica in gel form) (P-SG) extracted from the first adsorbent (RHA) using alkaline treatment. These grafted resins as novel adsorbents were prepared by ^{60}Co gamma-rays irradiation of 25 kGy. Characterization of the new prepared adsorbents were investigated; swelling kinetics, ash content, FTIR, TGA & DTA, BET surface area and their ability for adsorption of some organic compound (Methylene Blue and *P*-Nitro-phenol from aqueous solution. It was found that: the swelling ratios take the following order: 28.55, 24.08 and 20.46% for P-SG, P and P-SP, respectively. The P-SP has the highest value of ash content 9.5%, and the BET surface areas were 8.5, 4.3 and 2.815 m^2/g for P-SG, P-SP and P, respectively. For the adsorption of MB, the maximum capacity (q_m) was 277, 171.5 and 174.2 (mg/g), but for adsorption of P-NP it was 51.1, 38.6 and 52.99 (mg/g) for P, P-SP and P-SG. Finally, the new prepared four adsorbents were investigated for adsorption of Gd(III). The results showed high adsorption capacity; 229.36, 206.61, 184.84 and 133.33 for P-SG, P-SP, P and RHA, respectively. From this study we can conclude that the prepared four adsorbents can be used for sorption of Gd(III) as well as some organic compounds from aqueous solution.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

With more and more widespread use of rare earths (REs) in a variety of fields, drastically growing RE have been released into the environment and exposed to humans over the past three decades. Aqueous solution containing Gd(III) ion, even at trace level, is believed to be a risk for human beings for example, about 100 μM Gd(III) may cause proliferation of human cervical carcinoma cells–HeLa cells and destroy the human primary peripheral lymphocytes, pneumocyte, etc. [1]. Gd(III) is one of lanthanide elements that are considered as fission products. It is utilized in control rods for nuclear reactors and nuclear power plants and is effective for use with neutron radiography and in shielding of nuclear reactors. Due to its high toxicity, highly efficient enrichment of Gd(III) as well as its removal from aqueous solutions is of extreme importance. Also, its removal or recovery is of most important in treatment of radioactive wastes because lanthanides are important fission product produced from irradiated nuclear fuel [2]. Numerous techniques for removal of RE ions from water have been proposed, including adsorption [3–6], ion exchange, liquid — liquid extraction, chemical precipitation

and membrane separation [7,8], etc. Among these methods, adsorption technique turns out to be a favorable and feasible approach for separation of RE and heavy metal ions owing to its simplicity, low cost and high efficiency [9–31]. In the adsorption technique different adsorbent materials are used. These materials include: activated carbon, ion exchange (organic and inorganic) resin, natural and synthetic materials and polymer.

Polymers can be prepared using chemical, thermal and ionizing radiation as an initiator. High energy ionizing radiation, like gamma rays has been used as an initiator to prepare different kinds of adsorbent materials [32]. The Radiation-Induced Graft Copolymerization (RIGC) as a method used for modification of polymeric materials has been broadly used over recent years. A great deal of work has been done during last decades to develop it. The purpose of RIGC is obtaining biocompatible polymeric materials for removal and separation of appreciate metals. Simultaneous irradiation method is a simple technique for preparation of graft copolymers. In this method the polymer backbone formed by irradiation of monomers [32–33]. Graft copolymerization initiated by gamma irradiation may be one of the most effective than conventional copolymerization method because it is easy to create radical sites on the polymer matrix and to bring in various functional groups onto these sites. Polymerization possesses potential to simplify the grafting

process and reduce the cost of production as no catalysts or additives are needed to initiate the reaction. So, it has many advantages over other conventional methods [34–35].

Graft copolymerization is a method of addition of new and desirable properties to silica without drastically affecting its basic properties. Grafting is known to improve the characteristic properties of the backbones. Large number of studies has been reported for the graft copolymerization of poly acryl amide onto silica obtained from rice husk ash [36–37]. Rice husk is an agricultural residue available abundantly in rice producing countries. It is a by-product of the rice milling industry. This by-product consists of 35% cellulose, 25% hemicelluloses, 20% lignin, and 14–25% ash which contains about 94% silica by weight [37]. The burning process often causes serious domestic and international environmental problem, so it is very important to solve the problem of smoke and waste produced. Rice husk can be converted into valuable products which can be used for several applications in industry [38]. It is one of the most silica rich raw materials containing about 80–89% silica. Silica is an inexpensive and polymorphs material [39].

The aim of this work is to investigate the RIGC of monomers onto the surface of silica prepared from rice husk ash in two forms: powder and gel form. Synthetic polymers were characterized using different techniques and investigated for adsorption of some organic compounds and Gd(III) from aqueous solution. Consequently, studying the possibility of prepared adsorbent materials to be used for treatment of different types of liquid wastes.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals and reagents used were of analytical grade purity and used without further purification.

2.2. Preparation of gadolinium solution

Gadolinium nitrate (Sigma) stock solution of 1000 ppm was prepared directly by dissolving a calculated weight in double distilled water. The sample was transferred to a measuring flask (250 ml) and the volume was adjusted. The concentration of gadolinium ions was determined spectrophotometrically by Arsenazo (III) (Fluka) method [40] using a Shimadzu model 1601 double-beam UV spectrophotometer.

2.3. Extraction of silica from rice husk ash

Rice husk ash (RHA) was prepared by carbonization of Rice Husk (RH) at 550 °C for 1.5 h. For extraction of the silica the RHA was stirred with a solution of concentration 4% KOH (Sigma) at a weight ratio of 1:10 (g/ml) RHA to solution and heated to boiling for 1 h. The mixture was left overnight, filtered and washed twice with distilled water at a ratio of 1:8. Addition of 10% HCl (ADWIC-Egypt) to the filtrate, until the pH of the solution reached 5–7, to precipitate the silica gel. The obtained silica was used in two forms: the first is as it is in the wet form (gel form), and the second is used after drying (powder form) in an oven at 110 °C for sufficient time till constant weight to produce silica powder [21]. Sample of the carbonized Rice husk ash (RHA) was used as one of the adsorbents under our study without any treatment.

2.4. Preparation of polymer and grafted copolymers

2.4.1. Preparation of polymer [P]

Poly acrylamide (PAM)-acrylic acid (AAc)-sodium styrene sulfonate (SSS) polymer (PAM-AAc-SSS) was synthesized by polymerization of PAAM with AAc and SSS as monomers and N,N′ methylene bisacrylamide (NMBA) as crosslinking agent. This polymer was prepared by using free radical polymerization. Herein, we have been used gamma ray in the preparation of this polymer. Depending on a previous

work [41], the optimum synthetic conditions were as follow: AAc 10 mL, PAM 3.3 g, SSS 0.5 g and cross linking agent 0.010 g.

All components were mixed in glass tubes and subjected to ^{60}Co gamma-rays irradiation of 25 kGy. After irradiation, the obtained grafted copolymers was cut into small pieces and washed by acetone for removal of excess of unreacted monomers [41], washed with double distilled water and dried in an oven at 80 °C.

2.4.2. Preparation of copolymer grafted on silica surface (powder and gel); (P-SP and P-SG)

Grafting copolymerization reactions were carried out by the addition of silica to different monomers as mentioned in the above section. After dissolving 0.6 g of the extracted silica powder in distilled water with addition of drop of sodium hydroxide, it was added to the mixture of PAm/AAc/SSS. In another tube, 6.6 g of silica gel to the mixture of PAm/AAc/SSS. The final mixture of each tube was taken under intensive steering in de-oxygenated water and then exposed to gamma ray irradiation of 25 kGy. The obtained grafted copolymers were washed with acetone in order to remove residual monomer then grafted copolymers were dried at 80 °C [124].

2.5. Characterization of the new prepared adsorbents

2.5.1. Fourier transforms infrared spectroscopy (FTIR)

FTIR spectra of the prepared adsorbents were recorded to identify the functional groups using the KBr disk method. In this concern, the adsorbent sample was thoroughly mixed with KBr as a matrix. The disk formed was examined in FTIR spectrophotometer in the range from 4000 to 400 cm^{-1} at Ain Shams University.

2.5.2. Scanning Electron Microscope (SEM)

The surface morphology was determined with scanning electron microscopy (SEM) of the type Jeol 6510A Model, Japan. The morphology and grain size of the particles were identified, operating with beams of primary electrons 20 keV.

2.5.3. Swelling kinetics

To evaluate the swelling kinetics, the dried adsorbents was immersed in water at pH 4, 7, 10 for 24 h at 25 °C. Swollen samples were weighed by an electronic balance, after wiping the excess surface liquid by filter paper. The swelling ratio (SR) was defined by following equation [21]:

$$SR = (W_t - W_d)/W_d \qquad (1)$$

where W_d is the weight (g) of the dried sample, and W_t is the weight (g) of the swollen sample, at time t.

2.5.4. BET surface area

The specific surface area, pore volume, and pore size distribution of the prepared adsorbents were determined using nitrogen adsorption/desorption isotherm at 77 K by Brunauer–Emmett–Teller (BET) equation on the Quantachrome Nova instrument, Model 184 Nova1000e series, USA. The analysis was done at Hot Laboratories Center, Egyptian Atomic Energy Authority.

2.5.5. Thermal analysis

Thermo-gravimetric and differential thermal analyses (TGA/DTA). Sample was heated in a platinum crucible from room temperature to 1000 °C. Simultaneous TGA/DTA was analyzed using a Shimadzu DTG-60/60H thermal analyzer, Japan in Hot Laboratories Center, Egyptian Atomic Energy Authority.

2.5.6. Elemental analysis

The elemental analysis of carbon (C), hydrogen (H), nitrogen (N) and oxygen contents of prepared adsorbents were analyzed using a CHNS

Table 1
Effect of adsorbent type on the % removal of Gd(III).

No.	Adsorbent	% removal of Gd(III)
1	Rice husk (RH)	24.64
2	Rice husk ash (RHA)	93.94
3	Desilicated Rice husk ash	72.08
4	Silica in gel form (SG)	32.7
5	Silica in powder form (SP)	100
6	P(polyAAm-AcA-SSS) (P)	100
7	Poly (PAM/AAc/SSS/silica powder) (P-SP)	100
8	Poly (PAM/AAc/SSS/silica gel) (P-SG)	100

Experimental condition [$V = 15$ ml, $m = 0.03$ g, $T = 25$ °C, $C_0 = 100$ mg l^{-1}, Time = 24 h, pH = 5.5].

analyzer (Perkin Elmer Series II 2400 in Hot Laboratories Center, Egyptian Atomic Energy Authority). Prior to the CHNS analysis, the adsorbent sample was dried overnight at about 110 °C and cooled in desiccators.

2.6. Sorption from solution

The different prepared adsorbents were tested for their feasibility to adsorb MB, P-NP and Gd(III). A known volume and concentration of adsorbate was mixed with known weight of each sample of the prepared adsorbents and shacked at room temperature for 4.5 h. The residual concentration of each solution was measured. The uptake of each sample was measured using the following equation:

$$\text{Uptake} = (C_o - C_e) \times (V/m) \ (\text{mg/g}) \tag{2}$$

where, C_o and C_e are initial and final concentrations of adsorbate, V is the volume of adsorbate solution (L) and m is adsorbent weight (g) and % removal was calculated from the following equation:

$$\%\text{Removal} = (C_o - C_e)/C_o \times 100 \tag{3}$$

3. Results and discussions

3.1. Adsorption of gadolinium (Gd(III)) from aqueous solution

The efficiency of all the prepared adsorbents was examined for adsorption of gadolinium. Each adsorbent has a significant efficiency for adsorption of gadolinium as shown in Table 1. The results obtained indicated that Rice Husk (RH) as a raw material has lower % removal than carbonized Rice Husk (RHA). Silica powder which prepared from rice husk Ash and used in preparation of copolymer shows a high efficiency for adsorption of Gd(III), but this high capacity is due to the high pH of the silica powder solution (pH 8.5) and Gd(III) ions precipitated above

pH 6.5. Therefore; rice husk, desilicated rice husk ash and silica in gel and powder form as adsorbents were excluded in this study. The two types of prepared copolymer [P-SP,P-SG] which have the same structure of the polymer but the difference is in addition of the extracted silica gel and silica powder to form grafted copolymer, shows higher efficiency for removal of gadolinium at low pH than RH and RHA.

Therefore, in the present study rice husk ash (RHA), polymer (P) and grafted copolymer on the surface of the silica (P-SP and P-SG) were selected from eight prepared samples (Table 1) to be used as an adsorbent. The characterizations of the four synthetic new adsorbents were discussed and feasibility of using such polymeric materials for adsorption of gadolinium was investigated.

3.2. Characterization of the different prepared adsorbents

3.2.1. FTIR analysis

Fig. 1 shows the FTIR spectra of rice husk ash (RHA) before and after sorption of Gd(III), respectively. The peaks between 800 and 459 cm^{-1} of RHA suggest the presence of Si—H bonds. The presence of Si—O—Si groups is indicated by the peaks at 1100 cm^{-1}. The peak at 1386 cm^{-1} is due to the bending of C—H groups and the peak at 1636.2 cm^{-1} is possibly related to the bending mode of adsorbed water molecule [42, 43]. The stretching frequency of >C=O carbonyl was observed by the absorption peak at 1650 cm^{-1} [44]. Bonded-OH stretching and the C—H stretching from CH$_2$ groups were observed at 2925.3 cm^{-1}. Stretching OH band region at 3424.8 cm^{-1}, is due to the silanol group (—SiOH) and to the water adsorbed on the surface. In comparison of the Fig. 1(b) with the data which expressed in Fig. 1a exhibit the formation of (SiO-M) and Fig. 1b shows that broad band 3326 cm^{-1}, this band may due to the silanol group (SiOH) and to the water adsorbed on the surface. Lowering may be due to formation of (SiO-M) for Gd(III) metal ion and interaction with silica gel between 1191 and 612. The band at 466 cm^{-1} may be due to metal oxide [45].

FTIR spectrum of P polymer is presented in Fig. 2. The absorption peaks at 1036.9 cm^{-1} and 1201.6 cm^{-1} represent symmetric and asymmetric stretching in O=S=O [42]. The beak at 1460 cm^{-1} may be due to the carboxyl —COOH groups of acrylic acid, the peak appears at 834.8 cm^{-1} indicates the presence of aromatic SP^2 C—H bending which belong to para disubstituted aromatic. The peak at 671.1 cm^{-1} confirms the presence of —S—O stretching bond, those at 1728 and 1661 cm^{-1} to ν(C=O) of acrylic acid and acrylamide units, respectively. In addition to the previous data in Fig. 2a, there are new bands appear due to grafting on the surface of silica (powder or gel form). Figs. 2a and 3 (a) contain the band at 3434.1 cm^{-1} is due to —OH stretching of carboxylic group overlapped with the —OH of silanol groups Si—OH on the surface of the silica in Figs.s 3 and 4 [43]. The broad band at 2361 cm^{-1} implies inter-molecular hydrogen bonding between
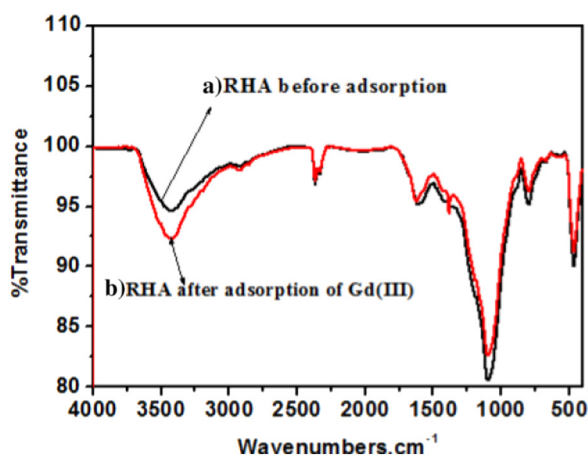

Fig. 1. (a, b) FTIR spectra of RHA before and after adsorption of Gd(III).
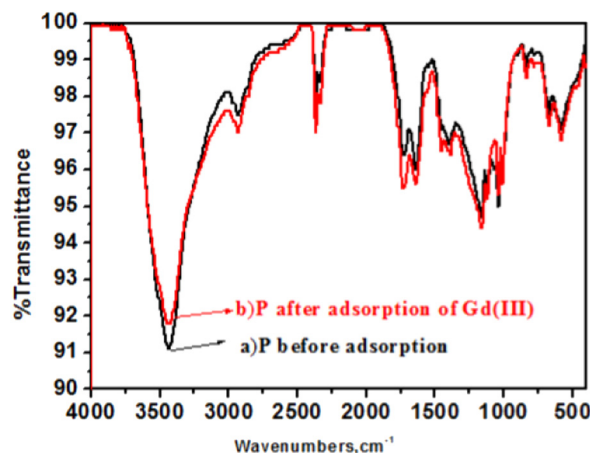

Fig. 2. (a, b): FTIR spectra of polymer (P) before and after adsorption of Gd(III).
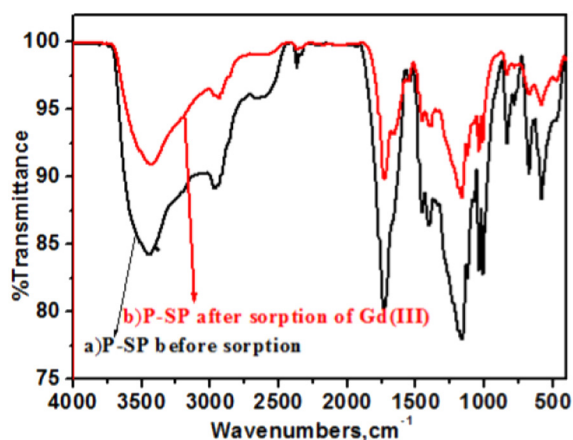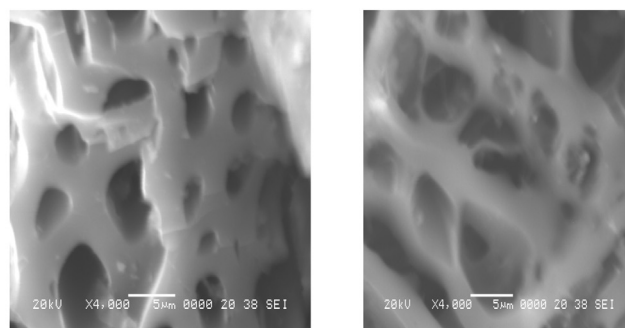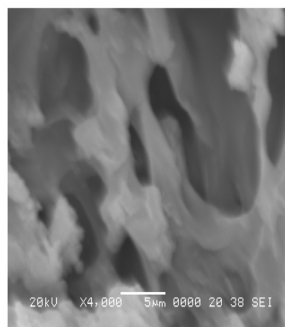
Fig. 3. (a, b): FTIR spectra of copolymer (P-SP) before and after sorption of Gd(III).

sulfonic acid and amide group [44]. The strong absorption band around 3434.1 cm^{-1} is attributed to the stretching of hydrogen-bonded hydroxyl groups (—OH) and amide groups.

Fig. 2b, 3b and Fig. 4b show that the difference of metal (Gd) - loaded polymer from the prepared polymer, the disappearance of absorption band of carboxylate (—COO). A new band at 407 cm^{-1} is present in the spectrum of P(AAm-AA-SSS)-M complex, which corresponds to —O—M—O— stretching [46] on the other hand the lower of intensities of all absorption band. The disappearance of carboxylate at 1542 cm^{-1}. Appearance of band at 1644 cm^{-1} may be due to interaction of (—C═O) of acrylic acid with gadolinium ions. Splitting of the band at 2350 cm^{-1} may be due to interaction of (—SO$_3$H) of SSS to form (—SO$_3$-M). The band at 473 cm^{-1} may be due to formation of P(AAm-AA-SSS-silica in powder form)-M complex. The intensity of the band at 2928 cm^{-1} may be due to silanol group interaction with the metal ions [46]. Fig. 2(b) shows that the intensity of carboxylic groups increased, this may be due to release of (—OH) and form complex with P polymer. It may form a complex with amide group, carboxylate as this band (1542 cm^{-1}) and sulfonate group (SO$_3$H) at 1122, 1066, 1036 cm^{-1}.

Fig. 3b shows that the splitting of the band of 2925 cm^{-1} indicating interaction of (CONH$_2$) of poly acrylamide, (C═N) or COOH) with M. The intensity of 2360 and 2339 cm^{-1} decreased, this may be due to formation of (—SO$_3$-M). Shifting of the band responsible for carboxylate to form (—COO-M) at 1558 cm^{-1}. The beak was shifted from 1734 to 1728 cm^{-1} and this may be due to interaction of (—C═O) with gadolinium ions.

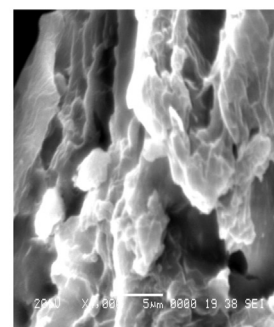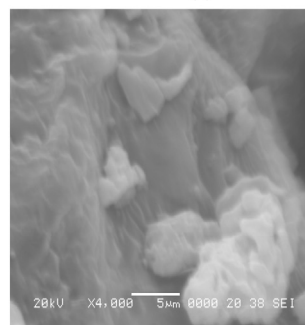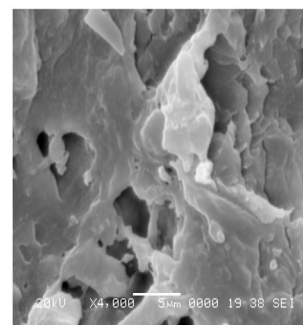**Fig. 4.** (a, b) FTIR spectra of polymer (P-SG) before and after sorption of Gd(III).

Fig. 5. SEM of the new prepared adsorbent materials: (a) RHA, (c) P, (e) P-SP and (g) P-SG before sorption of metal ions. b) RHA, (d) P, (f) P-SP and (h) P-SG after adsorption of Gd(III) ions.
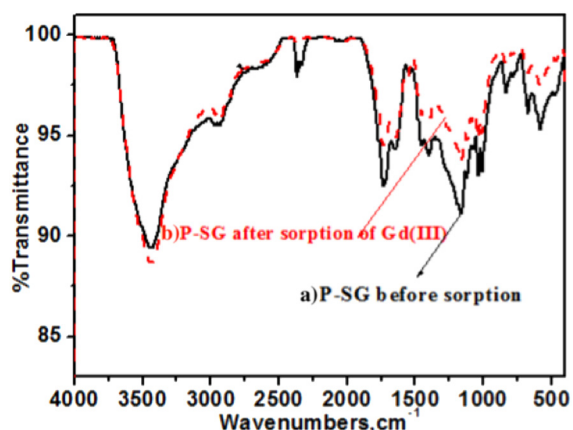
Appearance of band at 608 cm^{-1} and splitting of band to (672 and 582 cm^{-1}) may be due to interaction of silica to form metal complex. The appearance of new band at 407 cm^{-1} is present in the spectrum of P(AAm-AA-SSS-silica in gel form)-Gd complex as shown in Fig. 2b, which corresponds to —O—M—O— stretching [47]. The silanol group of silica gel and silica powder play a role in increasing uptake of the grafted copolymers.
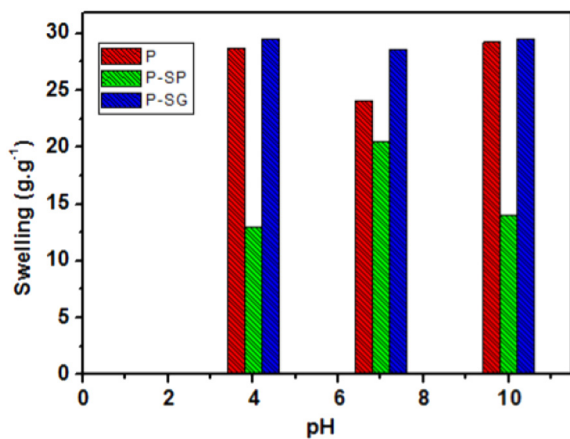
Fig. 6. Swelling percent of the prepared copolymer at different pHs.

3.2.2. Scanning electron microscopy (SEM)

Studies of the adsorbent's surface topography could provide important information on the degree of interaction between the sorbent particles and the metal ion species. In order to identify the morphological structures of the prepared sorbent after the preparation or modification process [48], SEM images for the produced sorbent materials were investigated as shown in Fig. 5. The images of the produced sorbent materials displayed a well pronounced porosity, with a series of irregular cavities distributed over the surface of all sorbent materials. Fig. 5(a), shows the pores which scattered on the surface of RHA. Fig. 5(c, e, g) shows the topography of P, P-SP and P-SG grafted copolymers. The pores and cavities showed by SEM constitute the surface area of the prepared sorbent which, in addition to functional groups, determines the capacity of sorbent material toward the pollutants present in aqueous solution [49]. Fig. 5(b) RHA shows a porous surface that metal ions interact with it. Polymers of good capacities, illustrated in Fig. 5(d, f and h) which showed that the copolymer have a porous structure appearance on the surfaces. It is supposed that pores are the regions of water permeation and interaction sites with the function groups of the copolymers that react with gadolinium ions.

3.2.3. Swelling kinetics

The ratio of swelling is one of the most important parameters that evaluating the properties of copolymers. Many structural factors such as; the charge, concentration, pKa of the ionizable group, degree of ionization, cross-linking density and hydrophilicity, influence the swelling of polymers. The properties of the swelling medium like the pH, temperature, ionic strength, counter ion and its valence affect the swelling characteristics [50]. The swelling ratio for the different prepared polymers at different pH values of 4, 7 and 10 was investigated and shown in Fig. 6 and Table 2.

The figure shows that the swelling of the polymers is affected by addition of silica where the addition of silica in gel form increases swelling ratio. But the addition of silica in powder form leads to decrease it. The swelling of polymers can be also affected by pH. The pH-responsive swelling behavior is basically due to ionization of the functional groups in the polymers [51], which changes on the pH of the surrounding

Table 2
The swelling ratio of the prepared grafted copolymers at different pHs.

Sorbent	Swelling		
	pH = 4	pH = 7	pH = 10
P	28.708	24.081	29.208
P-SP	13.0215	20.464	14.052
P-SG	29.478	28.549	29.5135

Table 3
BET surface area and pores properties of the prepared sorbent materials.

Sorbent materials	BET surface area (m²/g)	Total pore volume (TPV) (cc/g)	Average pore diameter (μm) (APR)
RHA	8.552	$1.8 * 10^{-2}$	42
P	2.815	$4.7 * 10^{-3}$	33.5
P-SP	4.3	$6.3 * 10^{-3}$	29
P-SG	8.5	$2.4 * 10^{-1}$	0.24

media from neutral to acid or base. P-SG still has the highest swelling in all medium indicating the suitability of this polymer for using in separation or treatment in all pH ranges, P-SG > P > P-SP.

3.2.4. BET surface area and porosity

Surface area and pore volume of the sorbent materials are factors which the sorption is greatly depending on. The specific surface area depends on particle size, particle shape and pores in the sorbent materials. It is clear that all of these factors have been responsible for giving a larger specific surface area to sorbent which in turn gives a large sorption capacity [52]. The surface area of rice husk ash is investigated. From Table 3, it was found that the surface area is 8.5 m²/g. From the IUPAC classification of sorption isotherms, the isotherm of RHA is of types IV with hysteresis and this indicates that RHA is mesopores (Fig. 7). Total pore volume is $1.8 * 10^{-2}$ cm³/g and majority of pore size distribution is mesoporous in addition to microporous.

The grafting of the polymer P on the surface of the silica increases the surface area from 2.8 to 4.3 and 8.5 for P-SP and P-SG, respectively. Table 3 shows that the surface area and pore volume of the prepared adsorbent materials are 2.815 and 4.3 for P and P-SP respectively. As silica facilitates the intervention of the particles inside the matrix of the polymeric copolymer which leading to increase the surface area. Polymer exhibits small specific surface area and pore volume and showed the non-porous characteristics and appreciable lowering of nitrogen sorption crystallinity, indicated that the interaction of the polymer is chemical not physical interaction [53]. The pore size distribution is few micro pores and macroporous and the majority is mesopores with total pore volume $4.7 * 10^{-3}$ cm³/g. P-SG has a high uptake (a large surface area and verity in pores). P-SG isotherm showing the hysteresis of Type V indicates bottle neck pores shape. P-SG has three types of pore size distribution mesopores, microporous and a very little macroporous.

3.2.5. Thermal analysis (TGA and DTA)

Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) play a vital role in studying the composition and the properties of any materials. TGA has been used in our study to investigate the decomposition characteristics of different new prepared sorbent materials. The TGA is the measurement of the weight change of a material as a function of temperature and time. The TGA-DTA curves of RHA sorbent which used as a source of silica are shown in Fig. 8. The first stage multi-step decomposition from 40 to 505 °C shows two endothermic peak at 64.28 and 223.34 °C which attributed to removal of all surface and matrix-bound moisture [48]. The weight loss in this region is 18.6%. The second stage from 505 to 850 °C exhibits a weight loss of 42.25% which due to loss of constitutive water, volatile materials and carbon combustion and become stable until 1000 °C. For poly(PAM/AAc/SSS) (P) polymer, TGA-DTA curves are shown in Fig. 9.

It can be seen that, the first stage from 50 to 179 °C with an endothermic peak at 74.69 °C exhibits a weight loss of 8.07% which due to the removal of absorbed water molecules. The second stage from (179 to 508.7)°C with a maximum endothermic peaks at 261–424–461 °C which exhibits a weight loss of 51.9% due to release of SO_2, water and NH_3 [48]. This decomposition occurred through a cyclization process with the removal of water molecules from two sulfonic, carboxylic (as a result of anhydride decarboxylation) and amide groups, respectively. The third stage from 508 to about 700 °C, shows exothermic peak at
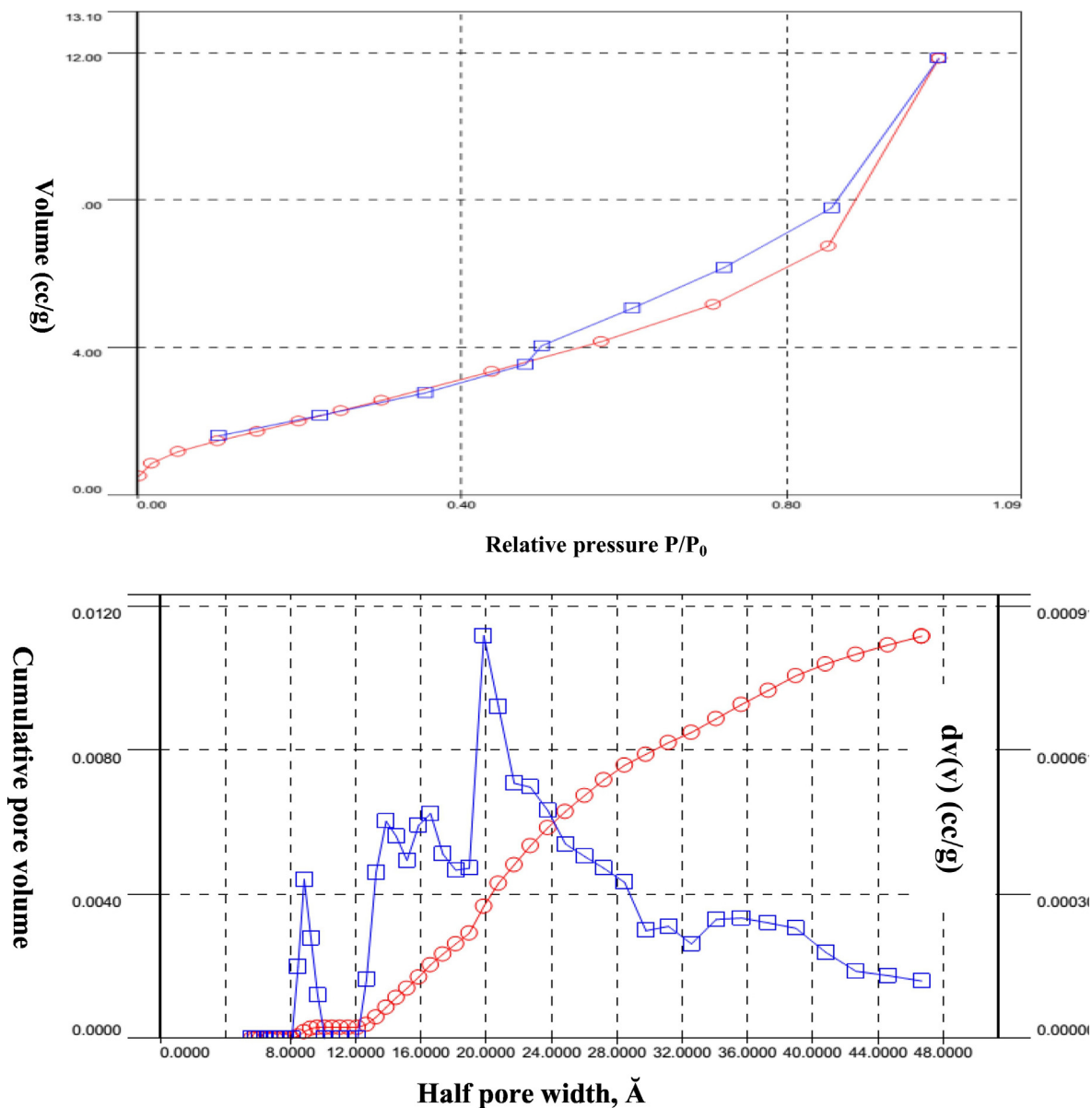
Fig. 7. The adsorption isotherm of N_2 and pore size distribution for RHA.

537.6 °C, exhibits a weight loss of 28.4% which due to removal of volatile hydrocarbons and complete degradation to the oxide form. The TGA and DTA curves for grafted copolymer poly (PAM/AAc/SSS/silica powder) (P-SP) are shown in Fig. 10.

It is clear that the degradation thermogram proceeds in multi-stages. The first stage from 53 to 302.5 °C with a maximum endothermic peak at 241.9 °C exhibits a weight loss of 37.38% which due to removal of physically absorbed water molecules [54]. The second stage from 300
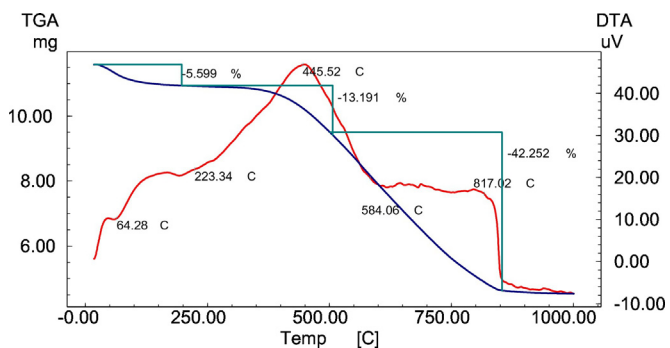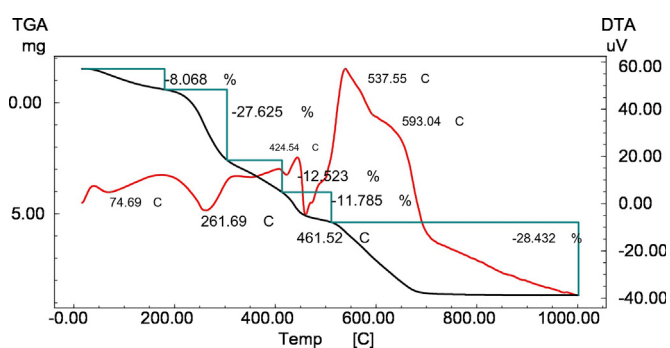

Fig. 8. DTA and TGA curves of RHA.

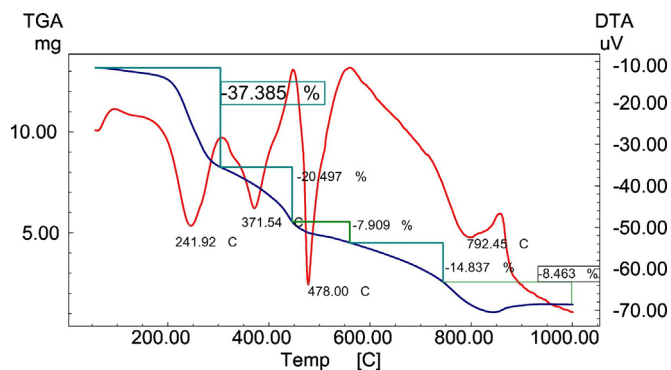**Fig. 9.** TGA and DTA curves of P polymer.

Fig. 10. TGA and DTA curves of P-SP.

Table 4
The ash content, density and elemental analysis for the prepared materials.

Adsorbent	C %	H %	N%	S %	O %	Ash content %	Density	
							Apparent	Packed
RHA	43.86	1.73	1.4	0.061	9.61	43.34	0.267	0.344
P	44.59	5.15	3.8	4.67	41.73	0.06	0.674	0.843
P-SP	44.59	5.19	2.87	3.49	34.36	9.5	0.926	1.019
P-SG	44.94	5.14	2.66	3.31	44.52	0.34	0.848	0.925

3.2.7. Density

The bulk density of a powder is its mass divided by the volume occupied by the powder. The volume includes the spaces between particles and volumes of the particles. Apparent density is defined as the mass of a unit volume, including pores and spaces between particles. Packed density of the material is the density of the powder when a fixed quantity of adsorbent is tapped in a standard closed measuring cylinder till the volume of the powder remains constant and does not decrease with further tapings [56], Table 4.

The apparent and packed density of polymer increased in presence of silica powder than in presence of silica in gel form. In all cases the apparent and packed density of prepared polymers are higher than those of the rice husk ash.

3.2.8. Ash content

Ash content of polymer P is low (0.06%) as it is prepared from organic material which decomposed at high temperature. The ash content increases as the silica present in grafted copolymers increases. In presence of silica as powder in P-SP polymer, ash content increases to (9.5%) due to presence of silica as silicon oxide, Table 4.

3.2.9. Sorption of some organic compounds

Sorption from solution is considered one of the most important factors for determination of the capacity of the prepared new sorbent materials and its affinity to adsorb organic dyes as the waste contains metal ions and organic materials such as dyes. Sorption of Methylene blue (MB), P-nitro-phenol (P-NP), iodine and phenol number are used generally for characterization of sorbent materials. In our study, we will concern with sorption of MB and P-NP for characterization of our new prepared sorbent materials.

3.2.9.1. Adsorption of methylene blue (MB).
As shown from Table 5, the presence of silica in preparation of copolymers decreases the uptake of MB dye. Generally, the obtained results indicated that the highest uptake of MB is obtained by the prepared sorbent materials took the following order: P > P-SP > P-SG > RHA. According to data, grafted copolymers were fitted to Langmuir isotherm model. And monolayer capacities were 227, 171.5 and 174.2 of P, P-SP and P-SG respectively. Separation factor (R_L) is between 0 and 1, indicating favorable sorption process. The n value in Freundlich equation of P, P-SP and P-SG was found to be 2.26, 5.8 and 2.38. It may be due to a distribution of surface sites or any factor that causes a decrease in sorbent-adsorbate

to 559.7 °C with a maximum endothermic peak at 371.5–478 °C exhibits a weight loss of 28.3% due to the decomposition of commoners and co-ordinated and uncoordinated amide groups. The third stage from 559.7 to 1000 °C with a maximum peak at 792.5 °C exhibits a weight loss of 23.2% which may be due to removal of silica and process accompanying by main chain scission, removal of volatile hydrocarbons and complete degradation to the oxides form [54].

The TGA and DTA curves of dried sample of poly (PAM/AAc/SSS/silica gel) (P-SG) is shown in Fig. 11, The first stage of four step decomposition started from 57 to 311 °C and shows the endothermic peak at 256.3 °C which attributed to removal of all surface and matrix-bound moisture from the polymeric materials, the weight loss in this region is 43.6%. The second stage from 311 to 581 °C exhibits a weight loss of 27.5% which due to the decomposition of amide groups [55]. This decomposition was carried out through a cyclization process with the removal of ammonia or water molecules from two amide and carboxylic groups. The third stage from 581 to 1000 °C showing a weight loss of 24.44% due to silica oxide, SO_2 and desulfonation of sulfonic acid and process accompanying by main chain scission, removal of volatile hydrocarbons and complete degradation to the oxide form [54].

3.2.6. Elemental analysis

Qualitative and quantitative elemental analyses of the prepared sorbent materials were carried out by the conventional methods used for low molecular weight compounds. Elemental analysis or determination of functional groups is especially valuable for copolymers or chemically modified polymers. Elemental analysis expressed in Table 4 illustrated that, the (C, H, N, S, O) % composition of the prepared polymeric materials are present in different percentage. The presence of nitrogen indicated the presence of amide group. The presence of sulfur indicated the presence of (SO_3H) in different percentages between the grafted copolymers.
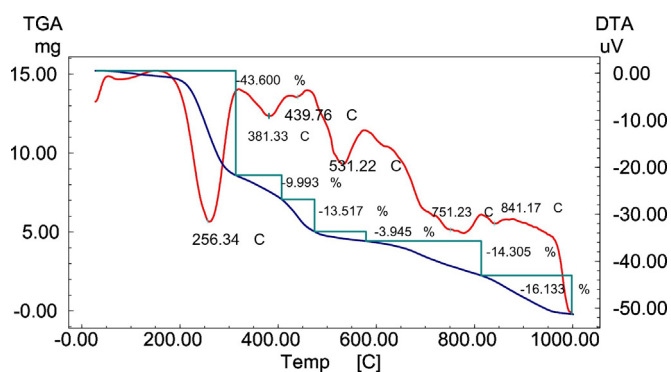

Fig. 11. DTA and TGA curves for P-SG.

Table 5
Parameters of Langmuir and Freundlich isotherms for sorption of MB.

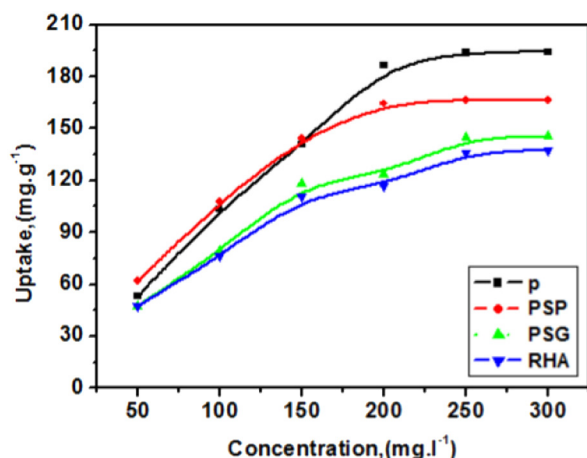| Isotherm models	Isotherm constants	Values for RHA	Values for P	Values for P-SP	Values for P-SG
Langmuir constants	Q_0 (mg/g)	–	227	171.5	174.2
	b (1 mg^{-1})	–	0.0499	0.2247	0.029
	R^2	–	0.9947	0.9991	0.9935
	R_L	–	0.950	0.816	0.029
Freundlich constants	K_f	1.25	26.3	73.6	17.8
	1/n	1.0	0.442	0.17	0.42
	n	1.0	2.26	5.88	2.38
	R^2	1.0	0.94	0.98	0.97

Fig. 12. The effect of concentration on the sorption of Methylene blue.

Fig. 13. Effect of P-NP concentration on the uptake of the prepared sorbent materials.

interaction with increasing surface density (Fig. 12). The n value was in the range of 1–10 representing good sorption of MB onto grafted copolymers [57–60].

3.2.9.2. Sorption of Para-nitrophenol (P-NP). RHA is slightly basic so, the uptake of P-NP onto RHA is higher than that of polymers (RHA > P > P-SG > P-SP). The dissociation of function groups of RHA gives (δ−ve) charge and P-NP is slightly acidic compound (has δ+ve charge), leading to attraction force between RHA and this phenol derivatives [61]. Data in Table 6 fitted with Langmuir isotherm as R^2 are 0.986, 0.987, 0.998 and 0.995 for RHA, P, PSG, P-SP respectively. The R_L value was found to be 0.99, 0.984, 0.984 and 0.99 of RHA, P, P-SP and P-SG respectively, indicating that the sorption of the adsorbate onto prepared sorbents is favorable (Fig. 13) [58].

3.3. Sorption of Gd(III)

In this part, the sorption of gadolinium ions was tested experimentally to investigate the sorption capacities of RHA, P, P-SP and P-SG grafted copolymers. In addition, to investigate the role of silica added to the prepared polymer on the sorption process of Gd(III) ions. Some factors affecting the sorption of the Gd(III) ions are studied. These factors are; contact time, hydrogen ion concentration (pH) and metal ions concentration.

3.3.1. Effect of shaking time

The contact time between the adsorbate and the adsorbent is of significant importance in separation process [62–63]. In order to evaluate the optimum contact time of sorption, effect of contact time was evaluated at different time intervals ranged from 15 min to 24 h, Fig. 14.

From this figure, it was found that the sorption of Gd(III) ions increased with increasing the shaking time until a steady state is attained after 4.5 h. At the initial stage, all the sorption sites are available and the Gd(III) ions can interact easily with these sites. So a high sorption rate is

obtained. Besides, the driving force for sorption is the concentration gradient between the bulk solution and the solid-liquid interface, and the concentration gradient is high in the initial period, which results in a high sorption rate [64–65]. The obtained data indicated that no significant change in the sorption is obtained after 4.5 h and this time was selected in the rest of the experimental work.

3.3.2. Effect of pH

The pH is one of the most important factor which influences solid phase surface dissociation, solution chemistry of the metal ions: hydrolysis, complexation, redox and precipitation reactions as well as the speciation and the sorption availability of the metal ion [12]. This significantly influences the sorption process and therefore pH should be optimized to ensure the best sorption capacity. The effect of pH in the range of 2 to 10 on the sorption of Gd(III) ions by the four selected sorbent materials (RHA, P, P-SP and P-SG) have been shown in Fig. 15. It shows that the uptake (mg/g) of the four new prepared sorbent materials is low at the lower pH values and increased with increasing the pH for all samples used. This finding may be accounted by the competitive sorption between H$^+$ ions and the Gd(III)ions for the same active sorption sites. Also at lower pH the surface of the RHA and the prepared grafted copolymers are slightly positive due to the sorption of H$^+$ which lead to electro repulsion force toward gadolinium ions (Gd(III)) and consequently decreasing the sorption of Gd(III) ions. As the pH increased, the positive charge at the surface decreased. This leads to the decrease of electrostatic repulsion between Gd(III) and H$^+$ and consequently the sorption capacities of the prepared sorbent materials are increased. The pH values (near pH = 6) are the optimum pH for the Gd(III) ions sorption. This is because above this pH value, Gd(III) ions

Table 6
Parameters of Langmuir and Freundlich isotherms for sorption of P-NP.

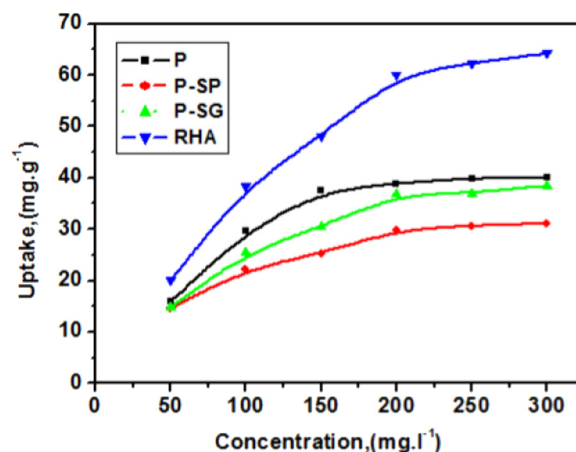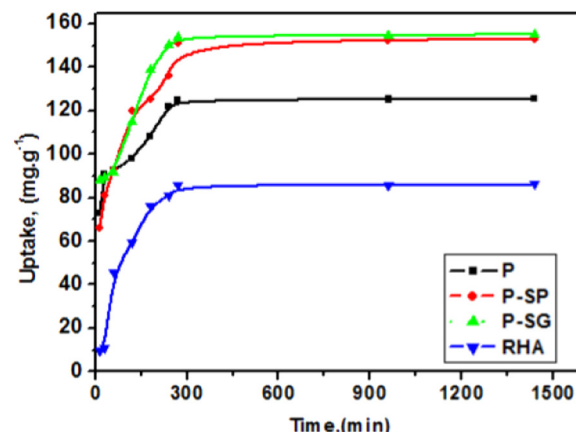| Isotherm models	Isotherm constants	Values for RHA	Values for P	Values for P-SP	Values for P-SG
Langmuir constants	Q_0 (mg/g)	97.40	51.10	38.60	53.0
	b (l mg^{-1})	0.0087	0.0162	0.0163	0.01
	R^2	0.986	0.987	0.998	0.995
	R_L	0.991	0.984	0.984	0.990
Freundlich constants	K_f	2.8	3.6	3.75	2.68
	1/n	0.588	0.455	0.389	0.494
	n	1.70	2.198	2.57	2.02
	R^2	0.97	0.927	0.980	0.976

Fig. 14. Effect of shaking time on the sorption of Gd(III) using new prepared sorbents.

Fig. 15. Effect of pH on the sorption of Gd(III) using new prepared sorbents.

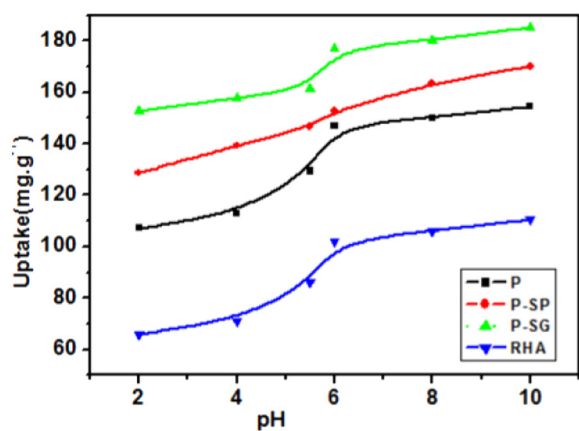Fig. 16. Effect of initial concentration on the uptake of Gd(III) using prepared sorbents.

start to precipitate. In addition, electrostatic attraction between the metal ions and the solid surface is increased at this pH value [6].

Table 7 shows that prepared polymer have effective function groups; amide, sulfonic, silanol and carboxylic that mainly affected on the adsorption process. The reaction mechanism of sorption of Gd(III) on the prepared sorbent materials is expected to be influenced by the presence of the effective functional groups; (carboxyl, sulfonic, amide, and silanol groups) since they are responsible for the metal immobilization in the sorption process [16]. In addition, the presence of silica may create an easily contact between the adsorbate and metal ions through the silanol group. This leads to increase of the surface area and total pores volume of the sorbent materials. This demonstrates the higher capacity of P-SP and P-SG than the other polymeric materials which is clear in Fig. 15.

The sorption equilibrium is dependent on the pH because it affects the dissociation of these groups (pK_a of carboxylic groups is about 4.8) [66], pK_a of amide groups is about 13.6 and pK_a of sulfonate groups is about −10 [66]. The extent of the carboxyl group and sulfonate group dissociation is higher as the value of pH increases, producing more free sites for Gd(III) ions sorption. The carboxyl groups, sulfonate groups, amide groups, silanol groups and hydroxyl groups present in the prepared copolymers (P, P-SP and P-SG) play a very important

role in metal sorption. They are being responsible for the metal immobilization in the sorption process [67]. Also it is reported that lanthanides appear to bind specifically to anionic groups in the matrix, possibly to the negatively charged groups [67]. The obtained results from Fig. 15 indicated that the maximum sorption capacity sequence of Gd(III) ions is in the order: P-SG > P-SP > P > RHA.

3.3.3. Effect of concentration of Gd(III)

The efficiency of sorption is a function of the initial concentration of adsorbate. The effect of initial Gd(III) ions concentrations (150–400 mg l^{-1}) on the sorption capacity of RHA and grafted copolymers was investigated and the results are shown Fig. 16. When the initial Gd(III) concentration increased from 150 to 400 mg l^{-1}, the sorption capacity increased from 85.52, 106.03, 120.31 and 60.02 mg/g to 124.255, 148.215, 155.15 and 86.125 mg/g for P, P-SP, P-SG and RHA, respectively.

The result showed that the sorption of Gd(III) is concentration dependent. For fixed sorbent dose the total available sorption sites are limited thereby adsorbing almost the same amount of the adsorbate [68–70], results in a decrease in percentage removal of the adsorbate corresponding to an increase in initial sorbate concentration. It can also be concluded that higher sorption efficiency at low concentration is important in terms of industrial application.

3.3.4. Sorption isotherm

Sorption equilibrium is usually described by an isotherm equation (whose parameters express the surface properties and affinity of the sorbent) at a fixed temperature and pH. Sorption isotherm describes the relationship between the amount of adsorbate on the sorbent and the concentration of dissolved adsorbate in solution at equilibrium [71]. In this concern, the sorption isotherms for Gd(III) ions onto different sorbent materials at room temperature were studied by applying Langmuir isotherm model, Table 8.

The value of maximum capacity Q_{max} corresponds to the monolayer coverage for a specific metal ion. The monolayer capacities are 133.33, 184.84, 206.61 and 229.36 mg/g for RHA, P, P-SP and P-SG, respectively. The value of R_L (separation factor) indicates the type of isotherm to be

Table 7
Structure of the constituents of the new prepared copolymer.

Poly acrylamide	Acrylic acid	Sodium 4-vinyl benzene sulphonate
$CH_2CHCONH_2$	$CH_2=CHCO_2H$	$C_8H_7NaO_3S$
Silica powder	**Silica gel**	

Table 8
Langmuir isotherm constants for the sorption of Gd(III) onto the prepared sorbents.

Isotherm model	Prepared sorbents	Values for RHA	Values for P	Values for P-SP	Values for P-SG
Langmuir constants	Q_0 (mg/g)	133.33	184.84	206.61	229.36
	b (l mg^{-1})	0.0173	0.043	0.0496	0.0445
	R^2	0.9914	0.9978	0.9998	0.9988
	R_L	0.1260	0.0550	0.0479	0.0532

Table 9
Comparison of q_{max} of Gd(III) for various sorbents.

Adsorbent	q_{max}, (mg/g)	References
Amberlite XAD4	4.44	[65]
Poly[Dibenzo-18-Crown-6]	89.9	[66]
MWAR resin	38.4	[67]
Dowex HCR-S/S	66.0	[68]
SBA-15–30%CsMVP	11.76	[69]
By-pass cement	100	[70]
Activated charcoal	114	[71]
1,2-HOPO-SAMMS	80	[72]
Polyethyleneglycol-(phosphomolybdate and tungstate) heteropolyacid	57	[73]
Rice husk ash (RHA)	133.33	This work
Poly (PAM/AAc/SSS) (P)	184.84	This work
Poly (PAM/AAc/SSS/silica powder) (P-SP)	206.61	This work
Poly (PAM/AAc/SSS/silica gel) (P-SG)	229.36	This work

irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). All the R_L values in Table 8 were found to be <1 and >0 indicating the favorable sorption process [72–75].

Table 9 represents a comparison of the sorption capacity of RHA, P, P-SP and P-SG obtained in this study with other adsorbents obtained in the literature for the sorption of Gd(III). From this table, it is obvious that our new prepared adsorbents; RHA, P, P-SP and P-SG show higher adsorption capacity for Gd(III) compared with other different adsorbents [75–80].

4. Conclusion

Silica in powder and gel forms has been extracted from rice husk ash and used for synthesizing different polymeric materials. Structural characterization of the prepared copolymers was performed by different analytical tools such as FT-IR, SEM, elemental analysis, swilling ratio, BET-surface area, thermal analysis (TGA and DTA) and adsorption from aqueous solution. Elucidation their properties and potential utilization for removal of organic and inorganic species from aqueous solutions has been investigated. The results revealed that these materials are efficient toward the uptake of methylene blue, *P*-nitro-phenol and the concerned metal ions n our study; gadolinium. 4.5 h is sufficient as contact time for adsorption of Gd(III) from aqueous solution of pH = 6 to obtain the maximum capacity from solution of concentration range (50–400 mg/l) by applying Langmuir isotherm. The maximum capacities are 133.33, 184.8, 206.61 and 229.36 mg/g for RHA, P, P-SP and P-SG, respectively. These values are higher than the other adsorbent used in adsorption of Gd(III) in literature. It can be concluded that the RHA, P polymer and P-SP and P-SG grafted copolymers are more economic and efficient for removal of rare earth elements than other adsorbents.

References

[1] W. Chen, L. Wang, Zhuo Mingpeng, Y. Liu, Y. Wang, Y. Li, Facile and highly efficient removal of trace Gd(III) by adsorption of colloidal graphene oxide suspensions sealed in dialysis bag, J. Hazard. Mater. 279 (2014) 546–553.
[2] C. Xiong, C.Y. Iran, Adsorption behavior of MWAR toward Gd(III) in aqueous solution, J. Chem. Chem. Eng. 29 (2010) 59–66.
[3] N.S. Awwad, H.M.H. Gad, M.I. Ahmad, H.F. Aly, Sorption of lanthanum and erbium from aqueous solution by activated carbon prepared from rice husk, Colloids Surf. B: Biointerfaces 81 (2010) 593–599.
[4] H.M.H. Gad, N.S. Awwad, Factors affecting on the sorption/desorption of Eu (III) using activated carbon, Sep. Sci. Technol. 42 (2007) 3657–3680.
[5] H.M.H. Gad, M.M.S. Ali, W.F. Zaher, E.A. El-Sofany, S.A. Abo-El-Enein, Application of olive stone based activated carbon in the sorption of lanthanum (III) ions from aqueous solution, Arab J. Nucl. Sci. Appl. 47 (2014) 67–79.
[6] H.M.H. Gad, S.I. El-Dessouky, A.A.M. Daifullah, A study of the factors affecting the removal of lanthanides from nitrate solution by activated carbon prepared from date pits, Int. J. Environ. Eng. Sci. 2 (1) (2011) 29–50.
[7] E.H. Borai, M.S. Abd El-Ghany, I.M. Ahmed, M.M. Hamed, A.M. Shahr El-Din, H.F. Aly, Modified acidic leaching for selective separation of thorium, phosphate and rare earth concentrates from Egyptian crude monazite, Int. J. Miner. Process. 149 (2016) 34–41.
[8] M.M. Hamed, M.A. Hilal, E.H. Borai, Chemical distribution of hazardous natural radionuclides during monazite mineral processing, J. Environ. Radioact. 162-163 (2016) 166–171.
[9] M. Daifullah, B.S. Girgis, H.M.H. Gad, Utilization of agro-residues (rice husk) in small waste water treatment plans, Mater. Lett. 57 (2003) 1723–1731.
[10] H.M.H. Gad, N.S. Awwad, A. El-Khalafawy, A.A.M. Daifullah, S.A. El-Reefy, H.F. Aly, Purification of industrial phosphoric acid using silica produced from rice husk (part 1), Arab J. Nucl. Sci. Appl. 43 (1) (2010) 65–74.
[11] H.M.H. Gad, T. El-Zakla, S.M. Yakout, Y.F. Lasheen, M.A. Rizk, Removal of radionuclides cobalt-60, and cesium-134 from contaminated solutions by sorption using activated carbon, Adsorpt. Sci. Technol. 29 (3) (2011) 331–344.
[12] H.M.H. Gad, E.H. Boraie, A. El-Khalafawy, Sorption and desorption of strontium using silica extracted from acid treated rice husk. I: Effect of pH and interfering ions, Arab J. Nucl. Sci. Appl. 45 (2) (2012) 142–154.
[13] H.M.H. Gad, Y.F. Lasheen, T.S. El-Zakla, Efficiency of local prepared activated carbon in the pre-concentration of barium-133 and radium-226 radionuclides in single and binary system, Radiochemistry 55 (6) (2013) 589–595.
[14] M.M. Hamed, M.M.S. Ali, M. Holiel, Preparation of activated carbon from doum stone and its application on adsorption of ^{60}Co and $^{152+154}$Eu: equilibrium, kinetic and thermodynamic studies, J. Environ. Radioact. 164 (2016) 113–124.
[15] H.M.H. Gad, A.M.A. Hassan, M.A. Mahmoud, T.F. Mohamaden, Treatment of liquid waste by sorption of toxic metal (Cr) using one-step steam pyrolysis corn cobs activated carbon, Int. J. Sci. Eng. Res. 5 (1) (2014) 1786–1800.
[16] H.M.H. Gad, T.F. Mohamaden, M.A. Mahmoud, Solid phase extractive pre-concentration of uranium (VI) from liquid waste onto peach stone steam pyrolysis activated carbon, Asian J. Chem. 28 (4) (2016) 751–760.
[17] H.M.H. Gad, Yasser F. Lasheen, Ayman F. Seliman, Sorption of Technetium-99 from low-level radioactive waste using different adsorbent materials, Asian J. Chem. 27 (12) (2015) 4479–4484.
[18] H.M.H. Gad, H.A. Omar, M.R. Hassan, M.H. Khalil, Factors affecting the sorption of Pb(II) from aqueous solutions using sawdust based activated carbon, J. Am. Sci. 9 (10) (2013) 95–106.
[19] H.M.H. Gad, Sh. Labib, M.M. Aly, Synthesis, characterization and application of nano-adsorbent materials in the sorption of Pb(II), Ni(II), Co(II), Mn(II), Li(I) from aqueous solution, J. Adv. Chem. 10 (8) (2014) 3053–3067.
[20] H.M.H. Gad, M.H. Khalil, M. Aziz, H.A. Omar, M.R. Hassan, Treatment of rice husk ash to improve adsorption capacity of cobalt from aqueous solution, Asian J. Chem. 28 (2) (2016) 385–394.
[21] H.M.H. Gad, Nabila A. Maziad, Radiation copolymerization of styrene/acrylic acid grafted to silica surface for separation and purification purposes: I. Characterization and sorption of some heavy metal and organic compounds, Int. J. Adv. Sci. Tech. Res. 4 (4) (2014) 184–201.
[22] H.M.H. Gad, H.A. Elsanafini, M.M.S. Ali, Y.F. Lasheen, M.G. Abdelwahed, Factors affecting the sorption behavior of Cs$^+$ and Sr^{2+} using biosorbent material, Russ. J. Appl. Chem. 89 (6) (2016) 988–999.
[23] V.K. Gupta, T.A. Saleh, Sorption of pollutants by porous carbon, carbon nanotubes and fullerene—an overview, Environ. Sci. Pollut. Res. 20 (5) (2013) 2828–2843.
[24] V.K. Gupta, D. Pathania, S. Sharma, S. Agarwal, P. Singh, Remediation of noxious chromium (VI) utilizing acrylic acid grafted lignocellulosic adsorbent, J. Mol. Liq. 177 (2013) 343–352.
[25] S. Agarwal, I. Tyagi, V.K. Gupta, M.H. Dehghani, R. Ghanbari, Investigating the residual aluminum elimination from conventional and enhanced coagulation by phosphate compounds in wastewater treatment process, J. Mol. Liq. 221 (2016) 673–684.
[26] T.A. Saleh, V.K. Gupta, Processing methods, characteristics and adsorption behavior of tire derived carbons: a review, Adv. Colloid Interf. Sci. 211 (2014) 93–101.
[27] V.K. Gupta, A. Nayak, S. Agarwal, Bioadsorbents for remediation of heavy metals: current status and their future prospects, Environ. Eng. Res. 20 (1) (2015) 1–18.
[28] H. Khani, M.K. Rofouei, P. Arab, V.K. Gupta, Z. Vafaei, Multi-walled carbon nanotubes-ionic liquid-carbon paste electrode as a super selectivity sensor: application to potentiometric monitoring of mercury ion (II), J. Hazard. Mater. 183 (1) (2010) 402–409.
[29] V.K. Gupta, S. Agarwal, T.A. Saleh, Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal, J. Hazard. Mater. 185 (1) (2011) 17–23.
[30] V.K. Gupta, S.K. Srivastava, D. Mohan, S. Sharma, Design parameters for fixed bed reactors of activated carbon developed from fertilizer waste for the removal of some heavy metal ions, Waste Manag. 17 (8) (1998) 517–522.
[31] T.A. Saleh, V.K. Gupta, Column with CNT/magnesium oxide composite for lead (II) removal from water, Environ. Sci. Pollut. Res. 19 (4) (2012) 1224–1228.
[32] A.A. El-Zahhar, H.M. Abdel-Aziz, T. Siyama, Gamma radiation-induced preparation of polymeric composite sorbents and their structure assignments, J. Macromol. Sci. A 44 (2007) 215–222.
[33] M. Jithunsa, K. Tashiro, S. Chirachanchai, Poly(acrylic acid-co-4-vinylimidazole)/sulfonated poly(ether ether ketone) blend membranes: a role of polymer chain with proton acceptor and donor for enhancing proton transfer in anhydrous system, Int. J. Hydrog. Energy 36 (2011) 10384–11039.

[34] B.L. Rivas, B. Urbano, C. Munoz, Metal ion sorption properties of water-insoluble resins based on sodium styrene sulfonate and different comonomers, Polym. Bull. 68 (2012) 1537–1549.

[35] D. Pathania, R. Sharma, S. Kalia, Graft copolymerization of acrylic acid onto gelatinized potato starch for removal of metal ions and organic dyes from aqueous system, Adv. Mater. Lett. 3 (2012) 259–264.

[36] E.S. Abdel-Halim, Preparation and characterization of poly (acrylic acid)-hydroxy ethyl cellulose graft copolymer, Carbohydr. Polym. 90 (2014) 930–936.

[37] K. Yoshinaga, T. Yokoyama, Y. Sugawa, N. Karakawa, H. Enomoto, M. Nishida, Cationic graft-polymerization of 2-methyl-2-oxazoline on monodispersed polymer-coated ultrafine silica particles, Polym. Bull. 28 (1992) 1070–1079.

[38] R. Patil, R. Dongre, J. Meshram, Preparation of silica powder from rice husk, Journal of Applied Chemistry (IOSR-JAC) International Conference on Advances in Engineering & Technology 2014, pp. 26–29.

[39] Ajay Kumar, Kalyani Mohanta, Devendra Kumar, Om Parkash, Properties and industrial applications of rice husk: a review, International Journal of Emerging Technology and Advanced Engineering 2 (2012) 2250–2459.

[40] Marczenko, Spectrophotometric Determination of Elements, John Wiley & Sons, 1986 537–575.

[41] Qiao-ling Yu, Yan Yang, Jie Zhang, Synthesis of superabsorbent resin acrylamide-acrylic acid-sodium p-styrene sulfonate terpolymer, Petrochem. Technol. Appl. 30 (2012) 221–223.

[42] J. Res, Characterization of combinatorial polymer blend composition gradients by FTIR microspectroscopy, J. Res. Natl. Inst. Stand. Technol. 109 (2004) 219–231.

[43] J.L. Dwyer, M. Zhou, Polymer characterization by combined chromatography-infrared spectroscopy, Int. J. Spectrosc. 13 (2011).

[44] W.H. Zhang, X.D. Fan, W. Tian, Polystyrene/nano-SiO₂ composite microspheres fabricated by Pickering emulsion polymerization, preparation, mechanisms and thermal properties, Express Polym. 7 (2012) 532–542.

[45] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density, Academic Publishers, Dordrecht, The Netherlands, 2004 43(26).

[46] H.D. Urrows, H.A. Ellis, S.I. Utah, Absorbed metal ions as stabilizers for the thermal degradation of polyacrylamide, Polymer 22 (2008).

[47] R. Bhargava, S. Wang, L. Jack, FTIR Microspectroscopy of polymeric systems, Adv. Polym. Sci. 163 (2003) 137–191.

[48] M. Chen, L. Wu, S. Zhou, Handbook of polymer nanocomposites. Processing, performance and application, Macromolecules 37 (2004) 613.

[49] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. 97 (2003) 219–243.

[50] V.A. Lee, R.G. Craig, F.E. Filisko, R. Zand, Preparation and characterization of high-surface-area polymer substrates for microcalorimetry, J. Appl. Polym. 28 (2001) 343–351.

[51] M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, Polymer Nanocomposite dielectrics – the role of the interface, J. Appl. Polym. 28 (2008) 343–351.

[52] C. Wang, J. Yan, X. Cui, H. Wang, Synthesis of raspberry like monodisperse magnetic hollow hybrid nanospheres by coating polystyrene template with Fe₃O₄, SiO₂ particles, J. Colloid Interface Sci. 354 (2011) 94–99.

[53] C. Wang, J. Yan, X. Cui, H. Wang, Synthesis of raspberry like monodisperse magnetic hollow hybrid nanospheres by coating polystyrene template with Fe₃O₄, SiO₂ particles, J. Colloid Interface Sci. 354 (2011) 94–99.

[54] P. Suzana, N. Kohji, T. Manita, Poly(acrylic acid-co-4-vinylimidazole)/sulfonated poly(ether ketone) blend membranes, Int. J. Hydrog. Energy 36 (2011) 10384–10391.

[55] K. Yoshinaga, T. Yokoyama, Y. Sugawa, N. Karakawa, Cationic graft-polymerization of 2-methyl-2-oxazoline on monodispersed polymer-coated ultrafine silica particles, Polym. Bull. 28 (2002) 1070–1079.

[56] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2004 326–338.

[57] H.M.H. Gad, Mahmoud M.S. Ali, Hisham S. Hassan, Different techniques for enhancing the removal of methylene blue (MB) dye from aqueous solution, Arab J. Nucl. Sci. Appl. 46 (3) (2013) 84–98.

[58] V.K. Gupta, T.A. Saleh, Sorption of pollutants by porous carbon, carbon nanotubes and fullerene—an overview, Environ. Sci. Pollut. Res. 20 (5) (2013) 2828–2843.

[59] V.K. Gupta, A. Mittal, D. Jhare, J. Mittal, Batch and bulk removal of hazardous colouring agent Rose Bengal by adsorption techniques using bottom ash as adsorbent, RSC Adv. 2 (22) (2012) 8381–8389.

[60] T.A. Saleh, V.K. Gupta, Functionalization of tungsten oxide into MWCNT and its application for sunlight-induced degradation of rhodamine B, J. Colloid Interface Sci. 362 (2) (2011) 337–344.

[61] H.M.H. Gad, Ashraf A. El.sayed, Activated carbon from agriculture by-products for the removal of rhodamine-B from aqueous solution, J. Hazard. Mater. 168 (2009) 1070–1081.

[62] M.M. Hamed, Sorbent extraction behavior of a nonionic surfactant, Triton X-100, onto commercial charcoal from low level radioactive waste, J. Radioanal. Nucl. Chem. 302 (2014) 303–313.

[63] A.K. Jain, V.K. Gupta, A. Bhatnagar, Suhas, A comparative study of adsorbents prepared from industrial wastes for removal of dyes, Sep. Sci. Technol. 38 (2) (2003) 463–481.

[64] A.S. Poursani, A. Nilchi, A.H. Hassani, M. Shariat, A novel method for synthesis of nano-γ-Al₂O₃: study of adsorption behavior of chromium, nickel, cadmium and lead ions, Int. J. Environ. Sci. Technol. 5 (1) (2015).

[65] S. Karthikeyan, V.K. Gupta, R. Boopathy, A. Titus, G. Sekaran, A new approach for the degradation of high concentration of aromatic amine by heterocatalytic Fenton oxidation: kinetic and spectroscopic studies, J. Mol. Liq. 173 (2012) 153–163.

[66] H. Arı, Z. Büyükmumcu, T. Ozpozan, I. Ilhan, O. Bahadır, Vibrational and theoretical analysis of pentyl-4-benzoyl-1[2,4-dinitrophenyl]-5phenyl-1H-pyrazole-3-carboxylate, 23 (8) (2013).

[67] M.M. Hamed, M. Holiel, Z.H. Ismail, Removal of ¹³⁴Cs and ¹⁵²⁺¹⁵⁴Eu from liquid radioactive waste using Dowex HCR-S/S, Radiochim. Acta 104 (2016) 399–413.

[68] E. Farahmand, Adsorption of cerium (IV) from aqueous solutions using activated carbon developed from rice straw, Open J. Geol. 6 (2016) 189–200.

[69] T.A. Saleh, V.K. Gupta, Processing methods, characteristics and adsorption behavior of tire derived carbons: a review, Adv. Colloid Interf. Sci. 211 (2014) 92–100.

[70] V.K. Gupta, R. Kumar, A. Nayak, T.A. Saleh, M.A. Barakat, Adsorptive removal of dyes from aqueous solution onto carbon nanotubes: a review, Adv. Colloid Interf. Sci. 193-194 (2013) 24–34.

[71] M.M. Hamed, M. Holiel, I.M. Ahmed, Sorption behavior of cesium, cobalt and europium radionuclides onto hydroxyl magnesium silicate, Radiochim. Acta 104 (2016) 873–890.

[72] E.A. El-Sofany, Removal of lanthanum and gadolinium from nitrate medium using Aliquat-336 impregnated onto Amberlite XAD-4, J. Hazard. Mater. 153 (2007) (2008) 948–954.

[73] K.R. Mahanwar, S.R. Sabale, N.S. Madane, G.H. Nikam, B.S. Mohite, Reversed phase partition chromatographic separation of Gd(III) from hippuric acid on poly[dibenzo-18-crown 6], Chem. Sci. J. 27 (2011) 1–12.

[74] C. Xiong, C. Yao, Adsorption behavior of MWAR toward Gd(III) in aqueous solution, Iran. J. Chem. Chem. Eng. 29 (2010) 59–66.

[75] M.M. Hamed, S.E. Rizk, A.A. Nayl, Adsorption kinetics and modeling of gadolinium and cobalt ions sorption by an ion-exchange resin, Part. Sci. Technol. 34 (2016) 716–724.

[76] H. Aghayan, A.R. Khanchib, A.R. Mahjoub, Synthesis and characterization of cesium molybdovanado phosphate immobilized on platelet SBA-15: an efficient inorganic composite ion-exchanger for gadolinium ion sorption, Appl. Surf. Sci. 274 (2013) 7–14.

[77] H.H. Osman, S.A. Sayed, M.E.H. Shalabi, The removal of some rare earth elements from their aqueous solutions on by-pass cement dust (BCD), J. Hazard. Mater. 195 (2011) 62–67.

[78] R. Qadder, J. Hanif, M. Saleem, M. Afazl, Adsorption of gadolinium on activated charcoal from electrolytic aqueous solution, J. Radioanal. Nucl. Chem. 15 (1992) 155–165.

[79] G.E. Fryxell, G.A. Porter, K. Pattamakomsan, V. Sukwarotwat, W. Chouyyok, V. Koonsiripaiboon, J. Xu, K.N. Raymond, Novel sorbents for removal of gadolinium-based contrast agents in sorbent dialysis and hemoperfusion: preventive approaches to nephrogenic systemic fibrosis, Nanomed. Nanotechnol. 6 (2010) 1–8.

[80] L. Zhang, S.D. Ding, T. Yang, G.C. Zheng, Adsorption behavior of rare earth elements using polyethyleneglycol (phosphomolybdate and tungstate) heteropolyacid sorbents in nitric solution, Hydrometallurgy 99 (2009) 109–114.